



# Grain refining enables mixed $\text{Cu}^+/\text{Cu}^0$ states for $\text{CO}_2$ electroreduction to $\text{C}_{2+}$ products at high current density

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## ABSTRACT

The oxidation status of Cu-based materials have been proved to be essential to the catalytic performances of electrochemical  $\text{CO}_2$  reduction. The coexistence of  $\text{Cu}^+$  and  $\text{Cu}^0$  species is generally considered as the origin of superior catalytic performance, yet the  $\text{Cu}^+$  moieties are subject to reduction under negative potentials especially at high current density. In this work, we report a grain refining approach to tune the oxidation states of Cu-based catalysts by modulating the electron transfer during electrochemical  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ) process when the in-situ electroreduction of  $\text{Cu}^+$  species occurs.  $\text{Cu}_2\text{O}$  nanospheres with abundant grain boundaries exhibited lower electron conductivity compared with  $\text{Cu}_2\text{O}$  nanospheres with less grain boundaries, which can hinder the complete reduction of  $\text{Cu}_2\text{O}$  and maintain  $\text{Cu}^+$  species under high current densities. As a result, the multi-grain  $\text{Cu}_2\text{O}$  showed a maximum FE of  $\sim 79\%$  for  $\text{C}_{2+}$  products at a high current density of  $800 \text{ mA cm}^{-2}$ , notably surpassing the later. Experimental and theoretical analyses indicated that mixed  $\text{Cu}^+/\text{Cu}^0$  states of multi-grain  $\text{Cu}_2\text{O}$  during reaction, favoring the C-C coupling process towards  $\text{C}_{2+}$  products. This work demonstrates the feasibility to tune the real valence state of catalytic sites under operational conditions by nanostructure engineering.

## 1. Introduction

Electrochemical  $\text{CO}_2$  reduction is a promising technology to convert  $\text{CO}_2$  into multiple value-added products using sustainable solar or wind energy [1–3]. Cu-based electrocatalysts have been proven to produce quantities of multi-carbon hydrocarbons and oxygenated fuels ( $\text{C}_{2+}$  products) via electrochemical  $\text{CO}_2$  reduction reaction [4–7]. While the detailed reaction mechanism of  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ) on Cu-based electrocatalysts has not been elaborated clearly, the oxidation states and chemical valences of Cu have been known to strongly correlate with the catalytic performance [8–13]. Particularly, oxide-derived Cu catalysts have been reported to show improved activity and selectivity towards  $\text{C}_2$  products (ethylene and ethanol) compared with pristine Cu foil electrode [11,14–16]. It has been generally accepted that the presence of  $\text{Cu}^+$  species during  $\text{CO}_2\text{RR}$  process is the main reason for this superior catalytic performance [16,17]. Further experimental evidences indicated that the mixture of  $\text{Cu}^+$  and  $\text{Cu}^0$  enhances multi-carbon

production (especially  $\text{C}_2\text{H}_4$ ) from  $\text{CO}_2$  reduction [10–12,18,19]. Such observation has been supported by recent quantum mechanics calculation, which revealed that the synergy between surface  $\text{Cu}^+$  and  $\text{Cu}^0$ , rather than single-valence sites, significantly promoted both  $\text{CO}_2$  activation and CO dimerization, favoring the production of  $\text{C}_{2+}$  products [20].

However, copper oxides would be easily reduced to metallic  $\text{Cu}^0$  under  $\text{CO}_2\text{RR}$  condition, and regulating the oxidation state of Cu catalysts during electrolysis reminds a big challenge [21–24]. Heteroatom doping [12,18,25], alloying [26] and surface modification [9] have been demonstrated to create or preserve the  $\text{Cu}^+$  moieties thus promoting the generation of  $\text{C}_{2+}$  products. However, these strategies usually require precise control over the chemical compositions. Pulse electroreduction that can in-situ produce  $\text{Cu}_2\text{O}$  has also been reported to regulate the oxidation state of Cu foil during  $\text{CO}_2\text{RR}$  process [27], yet the mechanistic exploration and implementation in practical devices remain difficult due to the complicated reaction environment [28]. While

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reaction intermediates have been reported to stabilize surface oxide/hydroxide species on Cu foil [29], modulating the adsorption of intermediates demands precise design on the nanostructures of electrocatalysts [30]. Overall, existing methods to preserve the  $\text{Cu}^+$  species during  $\text{CO}_2\text{RR}$  are rather circumscribed, which limits the capability to tune the valence state of Cu-based catalysts.

Herein, we demonstrate a grain refining approach to tune the valence states of Cu-based catalysts by modulating the electron transfer for the in-situ electroreduction of  $\text{Cu}^+$  species during  $\text{CO}_2\text{RR}$ . As a proof of concept,  $\text{Cu}_2\text{O}$  nanospheres composed of small grains have been shown to maintain a mixed  $\text{Cu}^+/\text{Cu}^0$  states at high current densities during  $\text{CO}_2\text{RR}$ , enabling highly efficient  $\text{C}_{2+}$  products formation by  $\text{CO}_2\text{RR}$ . The abundant grain boundaries within the  $\text{Cu}_2\text{O}$  nanospheres would inhibit the complete reduction of  $\text{Cu}^+$ , and provide numerous defect sites as catalytic active centers. The  $\text{Cu}_2\text{O}$  nanospheres with abundant grain boundaries maintain a high FE of  $\sim 79\%$  and a maximum partial current density of around  $700 \text{ mA cm}^{-2}$  for  $\text{C}_{2+}$  products, in contrast to the  $\text{Cu}_2\text{O}$  nanospheres with few grain boundaries producing large quantity of  $\text{H}_2/\text{CH}_4$  under similar condition. The origins of the remarkable catalytic activity have been explicitly explored by both experimental and theoretical analysis, providing some design guidelines for valence modulation of electrocatalysts.

## 2. Experimental section

### 2.1. Materials and methods

#### 2.1.1. Materials

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ( $\geq 99.0\%$ ),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  ( $\geq 98.0\%$ ),  $\text{NaOH}$  ( $\geq 96.0\%$ ), L-Ascorbic acid ( $\geq 99.7\%$ ),  $\text{N}_2\text{H}_4 \cdot x\text{H}_2\text{O}$  ( $\geq 85.0\%$ ) were purchased from Sinopharm Chemical Reagent Co.,  $\text{KOH}$  ( $\geq 95\%$ ) was purchased from Macklin Biochemical Co., Ltd. Multi-walled carbon nanotubes (MWCNTs) were purchased from Xianfeng Nano Co., Ltd. (Nanjing, China) and carbon black (CB) was purchased from Cabot Corporation. All chemical reagents were of analytical grade and used without further purification.

#### 2.1.2. Synthesis of $\text{Cu}_2\text{O}$ -1

1 mmol  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  was dissolved in 40 ml deionized water to form transparent solution, then 200  $\mu\text{l}$  85%  $\text{N}_2\text{H}_4$  was slowly dropped into the solution under stable magnetic stirring for 25 mins. The mixture was centrifuged to collect the solid powder and washed with deionized water for twice and ethanol for once before drying in a vacuum oven at  $60^\circ\text{C}$  overnight.

#### 2.1.3. Synthesis of $\text{Cu}_2\text{O}$ -2

2 mmol  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was added into 40 ml 0.1 M  $\text{NaOH}$  solution under magnetic stirring. After that, 2 mmol L-Ascorbic acid was added into the blue mixture and kept magnetic stirring for 30 mins. The final mixture was centrifuged and the collected powder was washed with deionized water for twice followed by ethanol for once before drying in a vacuum oven at  $60^\circ\text{C}$  overnight.

### 2.2. Characterizations

The morphologies of two kinds of  $\text{Cu}_2\text{O}$  and their corresponding electrodes after electrochemical  $\text{CO}_2$  reduction (AECR) were studied using scanning electron microscopy (SEM) on a Phenom LE microscope equipped with an Energy Disperse Spectroscopy (EDS). TEM images of two kinds of  $\text{Cu}_2\text{O}$  before and after  $\text{CO}_2\text{RR}$  was obtained using Jeol JEM-2100 F at the voltage at 200 KV. All the X-ray diffraction (XRD) patterns were obtained using Panalytical X'Pert3 X-ray Powder Diffractometer with  $\text{Cu K}\alpha$  X-rays. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha spectrometer using mono Al  $\text{K}\alpha$  source. UV-Vis spectra were recorded on SHIMADZU UV3600 ultraviolet and visible spectrophotometer under diffuse reflection mode.

The Brunauer–Emmett–Teller (BET) specific surface areas of samples were measured on a physical adsorption instrument Micromeritics ASAP2460. The Temperature Programmed Desorption (TPD) was conducted with AutoChem1 II 2920. Grain sizes of the  $\text{Cu}_2\text{O}$  nanospheres were determined by the Scherrer equation:  $D = K\lambda/(\beta\cos\theta)$ ; where  $D$  is the grain size that corresponding to the  $\text{Cu}_2\text{O}$  (111) direction;  $K$  value is usually equal to 1;  $\lambda$  is the wavelength of the X-ray;  $\beta$  is the half-height width of the specific diffraction peak and  $\theta$  is the diffraction angle.

### 2.3. Electrochemical evaluation

#### 2.3.1. Electrodes preparation

To prepare the gas diffusion electrodes (GDEs) used in the flow cell, 15 mg catalyst was mixed with 60  $\mu\text{l}$  5 wt% Nafion dispersion in 1.5 ml DI water and 2 ml ethanol. The mixture was ultrasonically dispersed for 30 mins to form homogeneous ink and 2 ml ink was air-brushed onto the hydrophobic gas diffusion layer ( $2.5 \text{ cm} \times 2.5 \text{ cm}$ ). The catalysts loading was estimated to be  $\sim 0.4 \text{ mg cm}^{-2}$  by weighing the GDE before and after catalysts deposition. To evaluate the redox behavior of different  $\text{Cu}_2\text{O}$ , the catalysts were directly deposited onto the glassy carbon (GC) electrodes. For the electrode preparation, 5 mg of catalyst was mixed with 20  $\mu\text{l}$  5 wt% Nafion dispersion in 250  $\mu\text{l}$  DI water and 250  $\mu\text{l}$  ethanol. After ultrasonic to form homogeneous ink, 10  $\mu\text{l}$  of the ink was pipetted onto the glassy carbon electrode with a diameter of 5 mm. The electrode was allowed to dry at ambient condition for further characterization. For the  $\text{Cu}_2\text{O}$ -2/CNTs or CB electrodes (both GDE and GC electrodes) with different carbon loading, the preparation process was mostly the same except that a different amount of MWCNTs/CB was added.

#### 2.3.2. Electrochemical $\text{CO}_2$ reduction

$\text{CO}_2$  electrolysis was conducted in 2 M  $\text{KOH}$  with our homemade three-compartment (gas, cathodic and anodic chambers) flow cell setup. The circular windows for electrolysis were set to be 16 mm for both the cathode and anode, yielding an activity area of  $2 \text{ cm}^2$ . The two chambers for catholyte and anolyte were made of polymethyl methacrylate (PMMA), each chamber had an inlet and an outlet for electrolyte to flow via a peristaltic pump. A  $\text{Hg}/\text{HgO}$  reference electrode was fixed in the catholyte chamber near to the cathode GDE to decrease the solution resistance ( $R_u$ ). The cathode GDEs were placed between the current collector and the electrolyte chamber with the microporous layer (MPL) facing the cathode electrolyte and a piece of Ni foam was used as anode directly facing the anode electrolyte. Silicone gaskets with a 16 mm diameter circular window were placed between GDE and the electrolyte chamber for sealing. An anion exchanged membrane (AEM, Fumasep FAB-PK-130) was used to separate the catholyte and anolyte chambers. All the pieces were pressed together by four pairs of screws and nuts at the four corners. Before  $\text{CO}_2$  electrolysis, the electrodes were activated by the CV method and  $R_u$  was measured by electrochemical impedance spectroscopy (EIS) analyses after activation using the Bio-Logic VSP potentiostat.  $\text{CO}_2$  electrolysis was conducted under different current densities using CHI 760e electrochemical workstation equipped with a current booster under chronopotentiometry mode. The potential converted to versus RHE with  $iR$  corrected was obtained by the following equation:

$$E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.0592 \cdot \text{pH} + 0.098 - iR_u$$

The gas outlet of the cathodic compartment was connected to an on-line gas chromatograph (GC9790Plus, FULI INSTRUMENTS) for analysis, which equipped with TCD detector to analyze  $\text{H}_2$  and FID detector to analyze CO and hydrocarbon products. Liquid products were analyzed via nuclear magnetic resonance spectroscopy (NMR) from respective catholyte solutions.  $^1\text{H}$  NMR spectra were collected on Bruker 400 M spectrometer in  $\text{D}_2\text{O}$  in water suppression mode using DMSO as the internal standard.

### 2.3.3. ECSA measurement

The ECSA of different electrodes was compared using the electric double-layer capacitance ( $C_{dl}$ ). To measure this, CV scans were recorded at different scan rates in the non-Faradaic potential region. The currents density at a given potential (usually the intermediate value of the non-Faradaic potential region) were recorded from the forward and reverse scans. The difference between these currents densities divided by two was plotted against the scan rate to obtain a straight line. The slope of this line corresponds to the capacitance of the catalyst's electric double-layer capacitance. Measurements were conducted under constant  $\text{CO}_2$  flow and recirculation of 2 M KOH electrolyte.

### 2.3.4. Half-cell energy efficiency

The calculation of the half-cell energy efficiency (EE) towards  $\text{C}_{2+}$  products of the two types of  $\text{Cu}_2\text{O}$  electrodes was based on the previous research.[31] In details, the calculations were conducted using the following equation:

$$\text{EE} = \sum (1.23 + (-E_{\text{C}_{2+}})) * \text{FE}_{\text{C}_{2+}} / (1.23 + (-E))$$

where  $E_{\text{C}_{2+}}$  is the thermodynamic potential (vs. RHE) of  $\text{CO}_2$  electrochemical reduction to corresponding product;  $\text{FE}_{\text{C}_{2+}}$  is the measured Faradaic efficiency in percentage for individual product;  $E$  is the applied potential vs. RHE.

### 2.3.5. CO stripping

The electrochemical CO stripping experiment was conducted in 1 M KOH electrolyte with the catalyst-coated glassy carbon electrode. For details, the electrolyte was first bubbled with pure Ar (99.999%) for 20 min to drive out other gases. Then Ar was switched to pure  $\text{CO}$  (99.999%) for another 20 min while the potential of the electrode was held constant at  $\sim 0$  V (vs. RHE) to allow complete adsorption of  $\text{CO}$  onto the catalyst. At last, Ar was again purged into the electrolyte for 20 mins to remove excess  $\text{CO}$  followed by a CV sweep setup at 20 mV/s.

### 2.3.6. In-situ Raman spectra

In situ Raman spectra were recorded with a Renishaw InVia Reflex Raman spectrometer using a 633 nm excitation laser (17 mW). The photons were dispersed by a 1800 l/mm grating and collected by a spectrometer. Each Raman spectrum was collected by one acquisition for 20 s. To exhibit the real reaction condition of  $\text{Cu}_2\text{O}$  electrodes we used the in-situ Raman flow cell that can operate at relatively high current densities. Spectra were collected under different constant current density range from  $-50 \text{ mA cm}^{-2}$  to  $-250 \text{ mA cm}^{-2}$ . The electrolysis was held for 300 s for each current density and the signal was collected within the last 30 s. For the long-term surface status monitoring, a new electrode was employed and the current density was kept at  $50 \text{ mA cm}^{-2}$  with a sampling interval of 3 min. During test,  $\text{CO}_2$  gas was continuously purged into gas chamber behind the backside of GDE so that ample gas reactant supply could be ensured. The cathode and anode electrolyte were both 1 M KOH flowed via peristaltic pumps, and two chambers were separated by a piece of AEM.

## 2.4. DFT calculation

Density functional theory (DFT) calculations were performed by using the Vienna ab initio simulation package (VASP), using the plane-wave basis with an energy cutoff of 500 eV, the projector augmented wave (PAW) potentials. The generalized gradient approximation with the function of Perdew–Burke–Ernzerhof (GGA-PBE) was applied to describe the exchange–correlation function. Grimme's semiempirical DFT-D3 scheme of dispersion correction was adopted to describe the van der Waals (vdW) interactions. The convergence criteria of the residual Hellmann–Feynman force and energy during structure optimization were set to  $0.02 \text{ eV } \text{\AA}^{-1}$  and  $10^{-5} \text{ eV}$ , respectively. Cu (111) surface and the  $\text{Cu}_2\text{O}(111)/\text{Cu}(111)$  was modeled with 20  $\text{\AA}$  vacuum to ensure no

interaction between two adjacent slabs. The Brillouin zone was sampled using  $2 \times 2 \times 1$  k-mesh for the calculation.

The change of Gibbs free energy for each step was calculated as the following equation:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} + \Delta G_{\text{field}}$$

where  $\Delta E$ ,  $\Delta \text{ZPE}$  and  $\Delta S$  are the difference in DFT-calculated total energy difference between the reactant and the product, contributions of the zero-point energy to the free-energy change and the change in entropy between the products and reactants, respectively.  $T$  is the temperature and taken as 298.15 K.  $\Delta G_U = -eU$ , where  $U$  is the electrode potential with respect to the standard hydrogen electrode and  $e$  is the transferred charge.  $\Delta G_{\text{pH}}$  is the correction  $\text{H}^+$  free energy by the concentration, which can be calculated through  $\Delta G_{\text{pH}} = k_B T \times \ln 10 \times \text{pH}$ , where  $k_B$  is the Boltzmann constant and  $\text{pH} = 0$  is assumed in the acidic medium in this calculation.  $\Delta G_{\text{field}}$  is the free-energy correction resulting from the electrochemical double layer, which is neglected in the present study.

## 3. Results and discussions

### 3.1. Characterization of $\text{Cu}_2\text{O}$ with different nanostructures

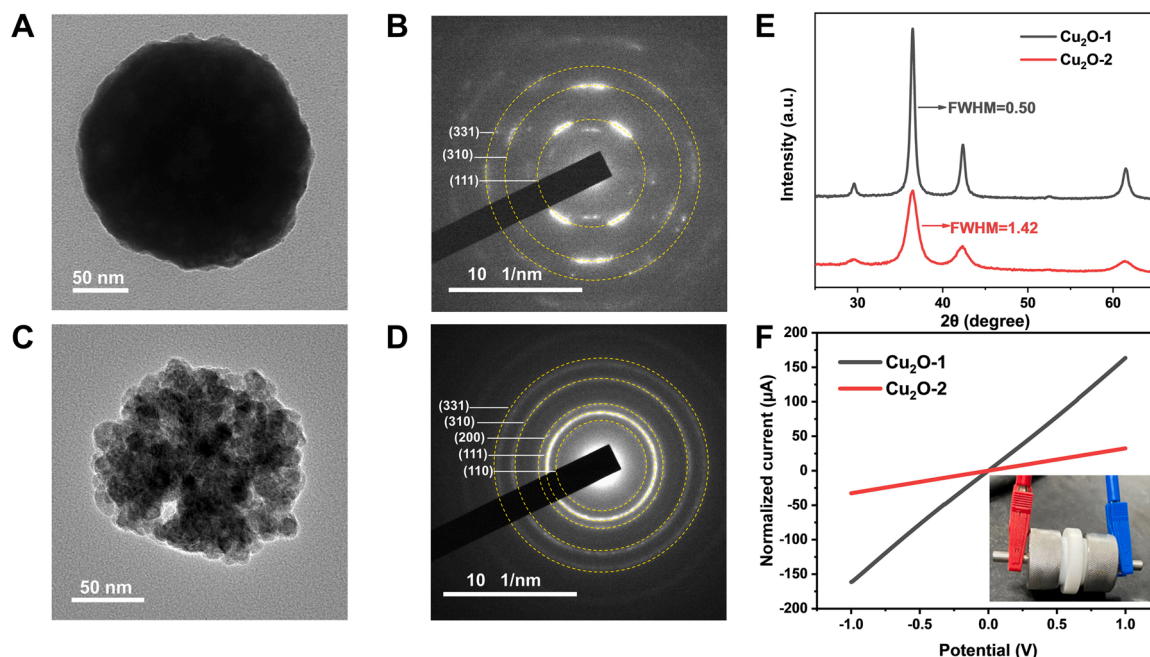
We first characterized the two types of  $\text{Cu}_2\text{O}$  nanomaterial with various technologies. The SEM images show that both types of  $\text{Cu}_2\text{O}$  were uniform nanospheres with a diameter of  $\sim 190 \text{ nm}$  (Figs. S1 and S2). The different texture of the two samples can be further observed in the TEM images.  $\text{Cu}_2\text{O}$ -1 nanosphere exhibits a solid texture (Fig. 1A), and the corresponding selected area electron diffraction (SAED) pattern consisted of discontinuous bright diffraction spots and weak diffraction rings (Fig. 1B). The high-resolution TEM (HRTEM) image reveals the continuous lattice fringes over a relatively large area in the particle (Fig. S3). In contrast,  $\text{Cu}_2\text{O}$ -2 nanosphere is highly porous and contains visible voids within the particle (Fig. 1C). The corresponding SAED pattern exhibits continuous strong diffraction rings, which indicated its polycrystalline nature with random grains orientation (Fig. 1D). Further observation showed that each  $\text{Cu}_2\text{O}$ -2 nanosphere consists of interconnected small nanocrystallites with lattice fringes belonging to different faces (Fig. S4). The XRD patterns further confirmed the pure  $\text{Cu}_2\text{O}$  phase of both samples (Fig. 1E). Grain sizes of the  $\text{Cu}_2\text{O}$  nanospheres were calculated to be 22.2 and 7.8 nm for  $\text{Cu}_2\text{O}$ -1 and  $\text{Cu}_2\text{O}$ -2, based on the strongest  $\text{Cu}_2\text{O}$  (111) diffraction peak using the Scherrer equation. Compared with  $\text{Cu}_2\text{O}$ -1, the porous texture and polycrystalline nature of  $\text{Cu}_2\text{O}$ -2 result in enlarged specific surface area as revealed by the  $\text{N}_2$  sorption isotherm (Fig. S5).

The above characterizations indicated that the two types of  $\text{Cu}_2\text{O}$  nanospheres exhibited distinct microstructures.  $\text{Cu}_2\text{O}$ -1 was consisted of relatively large nanocrystallites with preferred orientation while  $\text{Cu}_2\text{O}$ -2 was composed of smaller randomly oriented nanocrystallites. The smaller grain size endowed the latter with abundant grain boundaries that can alter the electron transfer behavior [32,33] which might further tune the oxidation states during the electro-reduction process. To verify this hypothesis, the electronic conductivities of two  $\text{Cu}_2\text{O}$  samples were tested via a simple voltammetry method (Fig. 1F). The much smaller current response of  $\text{Cu}_2\text{O}$ -2 compared with that of  $\text{Cu}_2\text{O}$ -1 indicated a lower electronic conductivity. The conductivity discrepancy can also be reflected by the different band gaps of the two  $\text{Cu}_2\text{O}$  samples [34], where  $\text{Cu}_2\text{O}$ -1 showed a slightly larger band gap (Fig. S6).

### 3.2. Electrochemical $\text{CO}_2$ reduction performances

The  $\text{CO}_2\text{RR}$  performance of the  $\text{Cu}_2\text{O}$  catalysts was evaluated in a flow cell setup under chronopotentiometry mode. The overall Faradaic efficiencies (FEs) of different  $\text{C}_{2+}$  products at various current densities were shown in Fig. 2A, which are mainly ethylene and ethanol as well as





**Fig. 1.** Characterizations of the Cu<sub>2</sub>O electrocatalysts. (A, C) TEM images and (B, D) SAED patterns of (A, B) Cu<sub>2</sub>O-1; (C, D) Cu<sub>2</sub>O-2. (E) XRD pattern showing the grain sizes difference and (F) Measurement of the electronic conductivity (insert showing the measuring setup).

a small amount of acetate and n-propanol (Figs. S7, S8). The Cu<sub>2</sub>O-1 exhibited the highest C<sub>2+</sub> FE of ~73% at a relatively low current density of 200 mA cm<sup>-2</sup>. At higher current densities the FEs of C<sub>2+</sub> products sharply decreased, while the FEs towards H<sub>2</sub> and CH<sub>4</sub> increased (Fig. S7). For Cu<sub>2</sub>O-2, the FEs for C<sub>2+</sub> products were low at low current densities and CO was the dominant CO<sub>2</sub> reduction product (Fig. S8). The FE towards C<sub>2+</sub> products increased with increasing current densities and reached the maximum of ~79% at 800 mA cm<sup>-2</sup> with C<sub>2</sub>H<sub>4</sub> as the main product. Negligible CH<sub>4</sub> was observed only at current density over 900 mA cm<sup>-2</sup> (Fig. S9). When referring to the C<sub>2+</sub> partial current density, Cu<sub>2</sub>O-2 showed a maximum of 692 ± 34 mA cm<sup>-2</sup> while only 330 ± 64 mA cm<sup>-2</sup> was achieved for Cu<sub>2</sub>O-1 (Fig. 2B). Since the two electrodes exhibited comparable electrochemical active surface areas (ECSAs) (Fig. S10), the higher C<sub>2+</sub> partial current density of Cu<sub>2</sub>O-2 suggested the presence of highly active sites for multi-carbon products. The reaction kinetics toward C<sub>2</sub>H<sub>4</sub> (the main C<sub>2+</sub> product) was further compared via Tafel analysis. The Tafel slopes were 90 and 141 mV dec<sup>-1</sup> for Cu<sub>2</sub>O-2 and Cu<sub>2</sub>O-1, respectively (Fig. 2C). The smaller Tafel slope indicated better reaction kinetics, which could be ascribed to the presence of highly active and efficient catalytic sites for C<sub>2</sub>H<sub>4</sub> [35].

Cu<sub>2</sub>O catalysts would be subjected to electroreduction during CO<sub>2</sub>RR, leading to oxide-derived Cu as the true electrocatalysts. The in-situ electroreduction of Cu<sub>2</sub>O catalysts was evaluated by cyclic voltammetry (CV) on a glassy carbon electrode. Both electrodes showed obvious reduction peaks within a potential range of -0.3 to -0.45 V vs. RHE, attributing to the reduction of Cu<sub>x</sub>O to Cu (Fig. 2D). The two oxidation peaks can be ascribed to the oxidation of Cu to Cu<sup>+</sup> and Cu/Cu<sup>+</sup> to Cu<sup>2+</sup>, respectively. Compared with Cu<sub>2</sub>O-2, the Cu<sub>2</sub>O-1 electrode exhibited more positive reduction potential and larger current density, indicating more pronounced reduction under negative potential and can be explained by its higher electronic conductivity as discussed earlier. This result suggested that the different microstructures of the two types of Cu<sub>2</sub>O might affect the oxidation state of Cu during electrolysis. Since the catalytic performance of Cu-based catalysts is highly related to the oxidation state, we speculate that the distinct catalytic performance was attributed to the different electroreduction behavior of Cu<sub>2</sub>O catalysts, which will be further discussed shortly.

Finally, the half-cell energy efficiency (EE) of two types of Cu<sub>2</sub>O

electrodes were further compared (Fig. S11). Under high current density, the EE of Cu<sub>2</sub>O-2 electrode was twice higher than that of Cu<sub>2</sub>O-1. For the stability of the catalyst, Cu<sub>2</sub>O-2 electrode maintained a high FE towards C<sub>2+</sub> products of over 73% within a long period, among which the FE of C<sub>2</sub>H<sub>4</sub> was about 45% (Fig. 2E). The FE of CO gradually decreased and CH<sub>4</sub> began to appear after 90 min electrolysis, indicating the dynamic composition (Cu<sup>+</sup> & Cu<sup>0</sup>) changes of the catalyst during reaction. In contrast, for Cu<sub>2</sub>O-1 electrode, the FE towards C<sub>2+</sub> products sharply decreased within a short period of time (Fig. S12). In term of electrocatalytic CO<sub>2</sub> conversion towards C<sub>2+</sub> products, the performance of Cu<sub>2</sub>O-2 is among the best reports in literature (Table S2).

### 3.3. Characterizations of the electrodes during and after CO<sub>2</sub>RR

To investigate the oxidation states and track the change of electrocatalysts during the CO<sub>2</sub>RR process, the electrodes were further characterized after the galvanostatic electrolysis at -800 mA cm<sup>-2</sup>. The solid spherical morphology of Cu<sub>2</sub>O-1 was generally preserved while the surface became rough (Fig. S13). As depicted in the HRTEM image, the Cu<sub>2</sub>O-1 AECR only showed continuous lattice fringes belonging to Cu (111), indicating the complete reduction to metallic Cu (Fig. 3A). This could be further verified by the SAED pattern that only shown the diffraction rings belonging to Cu (Fig. 3B). For Cu<sub>2</sub>O-2 AECR, the assembled nanospheres were partially collapsed (Fig. S14), and exhibited lattice fringes belonging to both Cu (111) and Cu<sub>2</sub>O (111) (Fig. 3C). The mixture state of Cu<sup>0</sup> and Cu<sup>+</sup> AECR was further confirmed by the SAED pattern (Fig. 3D). Despite the slight reconstruction of the electrocatalysts during electrolysis, the main micro-architectures were maintained. The different crystallographic compositions of the two types of Cu<sub>2</sub>O electrodes AECR were also confirmed by the XRD patterns, where metallic Cu and mixed Cu/Cu<sub>2</sub>O phases were identified for Cu<sub>2</sub>O-1 and Cu<sub>2</sub>O-2, respectively (Fig. S15).

The surface status of the electrodes before and after CO<sub>2</sub>RR was characterized by XPS. The Cu LMM Auger spectra indicated pure Cu<sup>+</sup> states of both electrodes before CO<sub>2</sub>RR (Fig. S16). After CO<sub>2</sub> electrolysis, the relative ratios of Cu<sup>+</sup>/Cu<sup>0</sup> were different for the two electrodes with the value 3.09 for Cu<sub>2</sub>O-1 and 4.40 for Cu<sub>2</sub>O-2 (Table S1 and Fig. S17). Despite the inevitable surface oxidation during sample transfer,<sup>34</sup> the

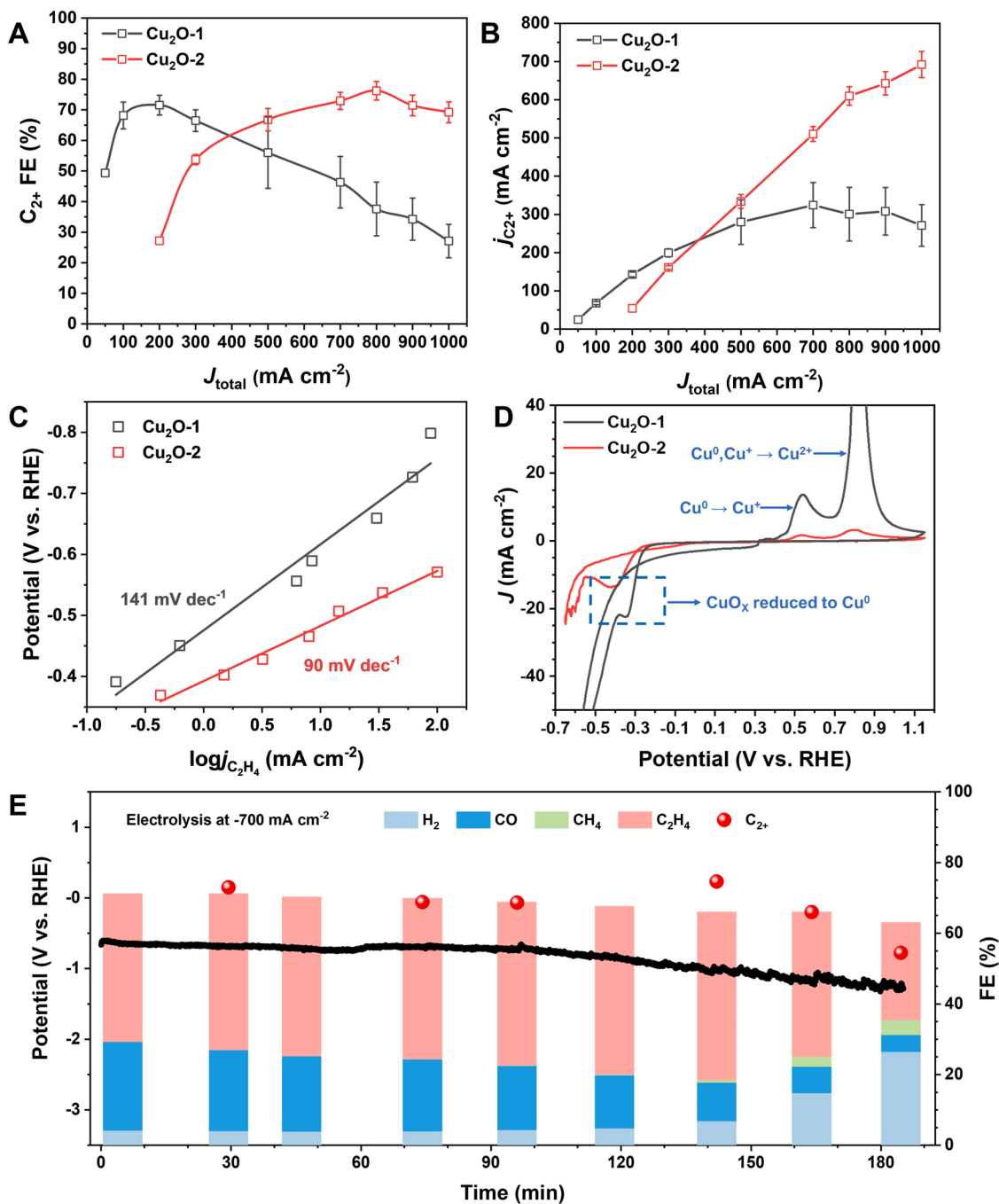
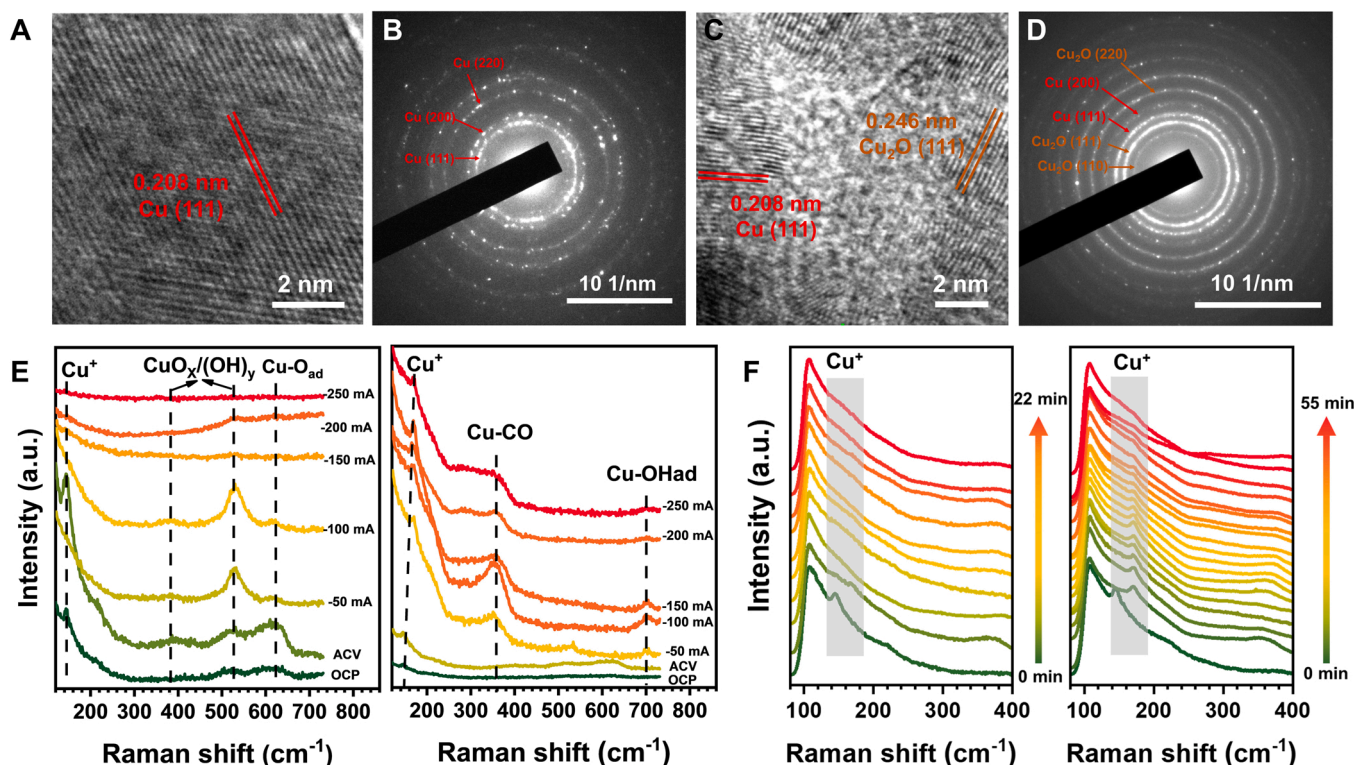


Fig. 2. Electrochemical CO<sub>2</sub> reduction performances of the Cu<sub>2</sub>O electrocatalysts. (A) FE of the overall C<sub>2</sub><sup>+</sup> products and (B) partial current densities of two electrodes under different current densities. (C) Partial C<sub>2</sub>H<sub>4</sub> current densities and Tafel slope of the two types electrodes. (D) Cyclic voltammetry (CV) curves of the two types of Cu<sub>2</sub>O. (E) Stability test of Cu<sub>2</sub>O-2 electrode under constant current electrolysis.

much higher Cu<sup>+</sup> content in the Cu<sub>2</sub>O-2 AECD indicated the better preservation of Cu<sup>+</sup> species during CO<sub>2</sub>RR.

In-situ Raman spectroscopic analysis was performed to monitor the surface species during CO<sub>2</sub>RR. For Cu<sub>2</sub>O-1 electrode, the Cu<sup>+</sup> band was only observed under open circuit potential (OCP) and after CV activation, which gradually vanished as current density increased (left panel in Fig. 3E). Interestingly, accompanied by the diminish of Cu<sup>+</sup> peak, the peaks assigned to CuO<sub>x</sub>/(OH)<sub>y</sub> (co-adsorption of OH and oxygen on metallic Cu) [29] and Cu-O<sub>ad</sub> [36] raised. This might be attributed to the rapid reduction of Cu<sub>2</sub>O to Cu that led to more adsorbed oxygenate species. For Cu<sub>2</sub>O-2, the Raman peak belongs to Cu<sub>2</sub>O was retained under current densities ranging from 50 to 250 mA cm<sup>-2</sup> (right panel in

Fig. 3E). Besides, a broad peak at ~350 cm<sup>-1</sup> also appeared, which could be ascribed to the Cu-CO stretch vibration [37,38]. Relatively weak band centered at ~700 cm<sup>-1</sup> was assigned to surface hydroxyl species on Cu (Cu-OH<sub>ad</sub>) [29]. For both electrodes, all the peaks decreased under high current densities, possibly due to the enhanced adsorption of \*H and rapid generation of gas that interfered the Raman signals. Time-dependent in-situ Raman spectra were further conducted to study the dynamic change of the surface/subsurface Cu species with time. For Cu<sub>2</sub>O-1 electrode, the Cu<sup>+</sup> peak intensity has decreased sharply within 1 min and completely vanished within 4 mins (left panel in Fig. 3F), which indicated a fast reduction process of Cu<sub>2</sub>O. In contrast, for Cu<sub>2</sub>O-2 electrode, the Cu<sup>+</sup> signal persisted after 50 mins with peak



**Fig. 3.** Characterizations of the Cu<sub>2</sub>O electrodes during and after CO<sub>2</sub>RR. HRTEM images showing the composition and structures of the electrodes (A, B) Cu<sub>2</sub>O-1 and (C, D) Cu<sub>2</sub>O-2. (E) In-situ Raman spectra monitoring the surface of the two electrodes under different current densities. Left for Cu<sub>2</sub>O-1 electrode and right for Cu<sub>2</sub>O-2 electrode. (F) Time dependent in-situ Raman spectra monitoring the dynamic changes on surface/subsurface. Left for Cu<sub>2</sub>O-1 electrode and right for Cu<sub>2</sub>O-2 electrode.

intensity gradually decreased with prolonged reaction time (right panel in Fig. 3F), which indicated its much more sluggish reduction kinetics. Obviously, the Cu<sub>2</sub>O-2 electrode would better preserve the Cu<sup>+</sup> species on the catalyst surface during electrolysis, thus maintaining mixed Cu<sup>+</sup>/Cu<sup>0</sup> states.

### 3.4. Mechanism exploration

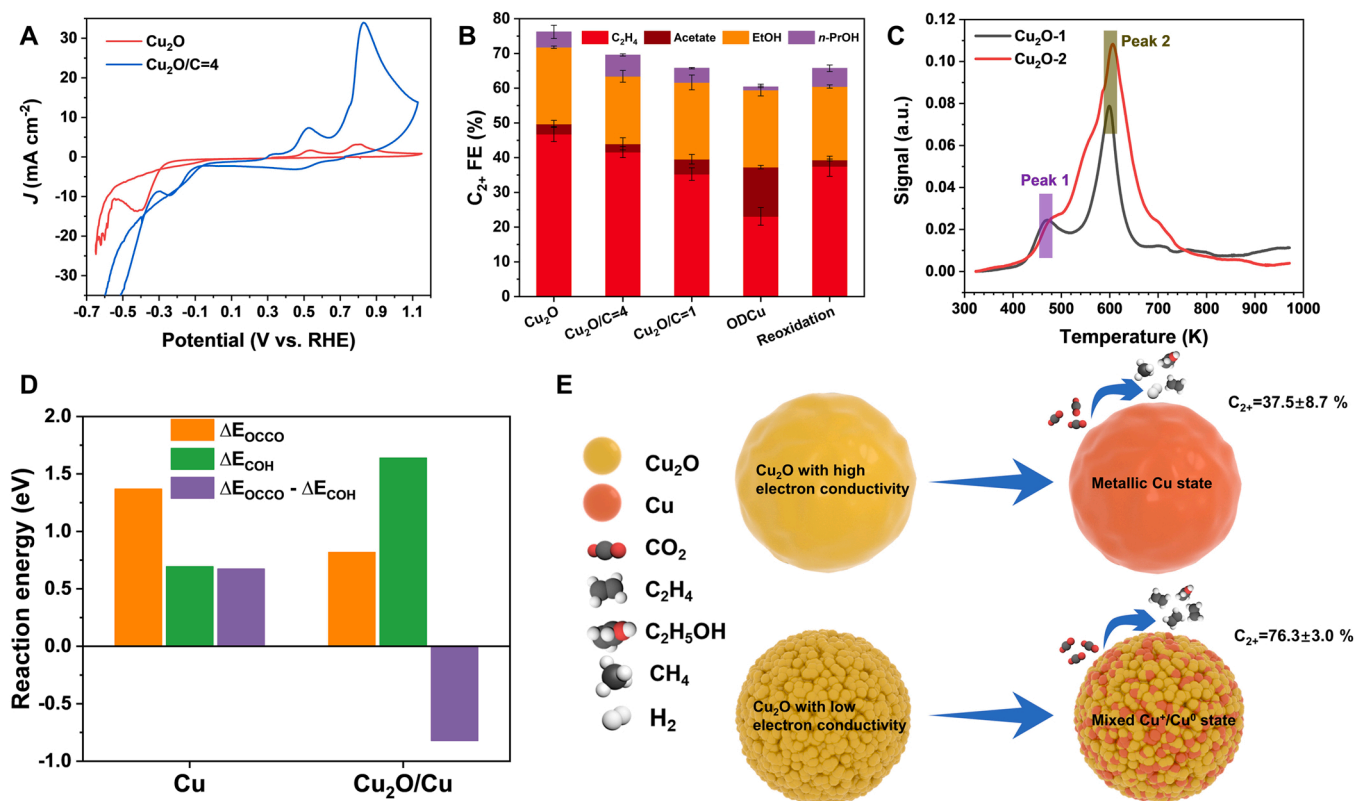
To verify that the dynamic change of Cu<sub>2</sub>O nanospheres (electroreduction of Cu<sup>+</sup> to Cu<sup>0</sup>) was governed by the electronic conductivity of the electrocatalysts, control experiments were performed by incorporating carbon nanotubes (CNTs) into the Cu<sub>2</sub>O-2 electrode. The highly conductive CNTs would modulate the electronic conductivity and thus affecting the redox behavior, as proved by the notably positive shifted reduction peak of Cu<sub>2</sub>O and more pronounced reversed oxidation peaks with a small amount of CNTs (Cu<sub>2</sub>O-2/C = 4, mass ratio) (Fig. 4A). Increasing the amount of CNTs leads to a further decreased total FE of C<sub>2</sub><sup>+</sup> products at a fixed current density of 800 mA cm<sup>-2</sup> (Figs. 4B, S18 and S19). Furthermore, pure CNTs electrode was inactive for CO<sub>2</sub>RR and mainly produced H<sub>2</sub> (Fig. S20). Other conductive carbons such as carbon black (CB) showed a similar effect on modulating the product selectivity (Fig. S21), again verifying that the dynamic evolution of electrocatalyst strongly depends on the conductivity [39]. If Cu<sub>2</sub>O-2 was pre-electrochemically reduced to oxide-derived Cu (ODCu), the C<sub>2</sub><sup>+</sup> FE was even lower (Fig. S22). The catalytic performance could be largely recovered when the ODCu electrode was re-oxidized. Similar to Cu<sub>2</sub>O-1 electrode, both Cu<sub>2</sub>O-2/CNTs and ODCu electrodes exhibited enhanced formation of H<sub>2</sub> and CH<sub>4</sub> (Fig. S23), which is in line with the low Cu<sup>+</sup>/Cu ratio during electrolysis (Fig. S24). While the ECSAs of the ODCu electrode was almost the same with that of Cu<sub>2</sub>O-2 electrode (Fig. S25), the different performance should be attributed to the different catalytic sites associating with the oxidation states. The different catalytic activity of Cu<sub>2</sub>O catalysts towards C<sub>2</sub><sup>+</sup> product is consistent with their Tafel slopes

of the corresponding partial current density. The Tafel slopes of the C<sub>2</sub>H<sub>4</sub> partial current densities were 111 and 138 mV dec<sup>-1</sup> for Cu<sub>2</sub>O-2/CNTs and ODCu, which were notably higher than that of Cu<sub>2</sub>O-2 (90 mV dec<sup>-1</sup>) (Fig. S26).

Based on the above discussion, we can conclude that the product selectivity of Cu<sub>2</sub>O electrocatalysts is highly related to the valence state of surface Cu sites, while the dynamic transformation of Cu<sup>+</sup> to Cu<sup>0</sup> during electrolysis would be affected by the microstructure of the catalysts. According to previous reports, Cu<sup>+</sup> dominated surface governs CO<sub>2</sub>RR towards CO/HCOOH [24,40], and Cu<sup>0</sup> dominated surface tends to produce H<sub>2</sub> and CH<sub>4</sub> [41,42]; only the coexistence of Cu<sup>+</sup> and Cu<sup>0</sup> sites favors the formation of C<sub>2</sub><sup>+</sup> products [11,19,20]. Thus, the dynamic evolution of Cu<sub>2</sub>O catalysts during electrolysis would explain the distinct electrocatalytic performance of the two electrodes. Specifically, at low current densities (equal to low overpotential) Cu<sub>2</sub>O-1 would be easily reduced to a mixture of Cu<sup>0</sup>/Cu<sup>+</sup> and achieve a high FE for C<sub>2</sub><sup>+</sup>; meanwhile, the Cu<sub>2</sub>O-2 would mostly preserve the Cu<sup>+</sup> species due to its resistance to electroreduction and favor the formation of CO. Further increasing the current density/overpotential leads to the complete reduction of Cu<sub>2</sub>O-1 to Cu<sup>0</sup> but a mixed Cu<sup>0</sup>/Cu<sup>+</sup> state for Cu<sub>2</sub>O-2, in line with the increased formation of CH<sub>4</sub> for Cu<sub>2</sub>O-1 and promoted C<sub>2</sub><sup>+</sup> formation for Cu<sub>2</sub>O-2.

Since CO is a key reaction intermediate for CO<sub>2</sub>RR, the binding strength between CO intermediate and electrocatalysts was investigated by CO temperature-programmed desorption (CO-TPD) (Fig. 4C). The Cu<sub>2</sub>O-1 exhibited two CO desorption peaks at 471.6 K (peak 1) and 598.7 K (peak 2) while the two peaks for Cu<sub>2</sub>O-2 were at 475.7 K and 605.6 K, respectively. The main desorption peak (peak 2) of Cu<sub>2</sub>O-2 at a higher desorption temperature indicated stronger binding with CO [43]. Enhanced CO adsorption has been reported on defects or low coordinated sites [44,45], and the abundant grain boundaries within the Cu<sub>2</sub>O-2 should be accounted for the enhanced CO binding, which can suppress HER and boost CO<sub>2</sub>RR process [44,46,47]. The quasi





**Fig. 4.** Mechanism exploration of the  $\text{Cu}_2\text{O}$  electrocatalysts. (A) Comparison of the redox behavior between  $\text{Cu}_2\text{O}$ -2 and  $\text{Cu}_2\text{O}$ -2/CNTs. (B) FE of the overall  $\text{C}_2^+$  products of  $\text{Cu}_2\text{O}$ -2-based electrodes with different compositions under  $800 \text{ mA cm}^{-2}$ . (C) CO-TPD of  $\text{Cu}_2\text{O}$  electrocatalysts. (D) DFT calculations showing the free energy related to the pathways of  $\text{CO}$  dimerization and  $\text{CO}$  hydrogenation on different surface. (E) Schematic diagram showing different micro-architectures tuning the oxidation state of  $\text{Cu}_2\text{O}$  electrocatalysts that eventually resulting in different catalytical performances.

adsorption quantity corresponding to each peak was shown in Fig. S27. The adsorption quantity (peak 2) of  $\text{Cu}_2\text{O}$ -2 was almost three times higher than that of  $\text{Cu}_2\text{O}$ -1. The enhanced  $\text{CO}$  adsorption on  $\text{Cu}_2\text{O}$ -2 further supported by electrochemical  $\text{CO}$ -stripping measurements (Fig. S28).

Density function theory (DFT) calculations were further conducted to explain the product selectivity of  $\text{CO}_2\text{RR}$  on Cu-based catalysts with different valence states. Dimerization and hydrogenation of  $\text{CO}$  have been regarded as the rate-determining step (RDS) toward  $\text{C}_2^+$  products and  $\text{CH}_4$ , respectively [48–51]. Therefore, the reaction pathways of  $\text{CO}$  dimerization and  $\text{CO}$  hydrogenation at Cu surface with different oxidation states were calculated (Figs. 4D and S29). At completely reduced  $\text{Cu}_2\text{O}$  (Cu metal),  $\text{CO}$  hydrogenation to  $\text{COH}$  was favored over  $\text{CO}$  dimerization. In contrast, for partly reduced  $\text{Cu}_2\text{O}$  (denoted as  $\text{Cu}_2\text{O}/\text{Cu}$ ) with mixture valence states of  $\text{Cu}^+/\text{Cu}^0$ , dimerization of  $\text{CO}$  was much favored. For the  $\text{CO}$  dimerization process, the Gibbs free energy ( $\Delta G$ ) at partly reduced  $\text{Cu}_2\text{O}$  was  $0.82 \text{ eV}$ , which was much lower than that on metallic Cu surface ( $\Delta G = 1.37 \text{ eV}$ ). These results indicated that coexistence of  $\text{Cu}^+$  and  $\text{Cu}^0$  can greatly lower the energy barrier for the C-C coupling process thus favoring  $\text{C}_2^+$  products, which is consistent with the experimental results. From the discussion above, we can conclude that the distinct catalytic performance between two types of  $\text{Cu}_2\text{O}$  can be attributed to the oxidation states and composition variation during  $\text{CO}_2\text{RR}$ . Through grain boundary refining, the electron transfer process can be modulated, which affects the true valence state and catalytic sites of electrocatalysts at operational conditions as schematically depicted in Fig. 4E.

#### 4. Conclusions

In summary, we report a grain refining approach to regulate the

valence states of Cu-based electrocatalysts during  $\text{CO}_2\text{RR}$ .  $\text{Cu}_2\text{O}$ -2 nanospheres with abundant grain boundaries exhibit a maximum FE of  $\sim 79\%$  for  $\text{C}_2^+$  products and a highest  $j_{\text{C}_2^+}$  of  $692 \pm 34 \text{ mA cm}^{-2}$ , much superior to the  $\text{Cu}_2\text{O}$ -1 with a solid texture. Such different catalytic performance has been mainly attributed to the distinct valence state of catalysts during electrolysis. Due to the retarded electron transfer by the grain boundaries,  $\text{Cu}^+$  species could be better preserved in  $\text{Cu}_2\text{O}$ -2 at high current densities during  $\text{CO}_2\text{RR}$  process as revealed by both in-situ and ex-situ characterizations. Besides,  $\text{CO}$  as a key intermediate would be better stabilized on the grain-boundary-rich  $\text{Cu}_2\text{O}$ -2 catalyst. DFT calculations confirmed that the coexistence of  $\text{Cu}^+/\text{Cu}^0$  species leads to decreased energy barrier for  $\text{CO}$  dimerization, thus promoting the formation of  $\text{C}_2^+$  products. The present work demonstrates an efficient strategy to regulate the valence state of the real catalytic active sites under operational conditions.

#### CRediT authorship contribution statement

**Xiangzhou Lv:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **Qian Liu:** Investigation, Formal analysis. **Jianghao Wang:** Investigation, Formal analysis. **Xiuju Wu:** Investigation, Validation. **Xiaotong Li:** Formal analysis. **Yue Yang:** Formal analysis. **Jianhua Yan:** Writing – review & editing. **Angjian Wu:** Methodology, Resources, Writing – review & editing. **Hao Bin Wu:** Conceptualization, Methodology, Funding acquisition, Writing – review & editing, Supervision, Project administration.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122272](https://doi.org/10.1016/j.apcatb.2022.122272).

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